UNIVERSITY OF CALIFORNIA, SANTA BARBARA

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO

SANTA BARBARA • SANTA CRUZ

Materials Department
Santa Barbara, CA 93106

Administrative Assistant, (805)893-7161

Timothy Deming
Assistant Professor
ph. (805) 893-8474
fax (805) 893-7221
tdeming@engineering.ucsb.edu

May 20, 1997

Office of Naval Research
Program Officer Michael T. Marron ONR 341
Ballston Centre Tower One
800 North Quincy Street
Arlington, VA 22217-5660

Dear Dr. Marron,

Enclosed please find 3 copies of the annual technical progress report for our grant # N00014-96-1-0729. If you need additional information, please feel free to contact me.

Sincerely,

Timothy J. Deming
Departments of Materials and Chemistry
University of California, Santa Barbara
Santa Barbara, CA 93106

CC: Administrative Grants Officer
Office of Naval Research Regional Office San Diego
4520 Executive Drive, Suite 300
San Diego, CA 92121-3019

Director, Naval Research Laboratory
Attn: Code 2627
4555 Overlook Drive
Washington, DC 20375-5326

Defense Technical Information Center
8725 John J. Kingman Road
STE 0944
Ft. Belvoir, VA 22060-6218

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31 May 1997	Performance Report 1 June 1996-31 May 1997

4. TITLE AND SUBTITLE

High Performance underwater adhesives: synthethic analogs of marine mussel cement proteins.

5. FUNDING NUMBERS

G
N00014-96-1-0729

6. AUTHOR(S)

Timothy J. Deming

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

Materials Department
University of California
Santa Barbara, CA 93106

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

Office of Naval Research
Ballston Centre Tower One
300 North Quincy Street
Arlington, VA 22217-5660

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release

12. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This annual progress report summarizes the progress made in the principal investigator's research program focused on synthesis of moisture-resistant adhesive polymers. Statistically random copolypeptides containing only 2 or 3 different amino acid components were found to be effective moisture-resistant adhesives. In addition to polymer composition, a key to successful adhesive bonding was the type of oxidant used to effect crosslink formation. We have begun to optimize the copolymer compositions and oxidizing conditions necessary for obtaining useful adhesive properties. The realization of effective moisture-resistant adhesion in simple copolymers provides a potentially valuable source of these materials which can be produced relatively inexpensively and in large quantities. We envision both industrial and biomedical applications for these polymers.

14. SUBJECT TERMS

marine adhesives, moisture-resistant adhesion, biopolymers

15. NUMBER OF PAGES

2

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	SAR

ANNUAL PROGRESS REPORT

Grant #: N00014-96-1-0729

PRINCIPAL INVESTIGATOR: Dr. Timothy J. Deming

INSTITUTION: University of California at Santa Barbara

EMAIL: tdeming@engineering.ucsb.edu

GRANT TITLE: High Performance Underwater Adhesives: Synthetic Analogs of Marine Mussel Cement Proteins.

REPORTING PERIOD: 1 June 1996 - 31 May 1997 (12 months)

AWARD PERIOD: 1 June 1996 - 31 May 1999

OBJECTIVE: To chemically synthesize and characterize polymeric materials possessing the characteristics of marine adhesive proteins which can be prepared in large scale with consistent composition and control over their physical properties.

APPROACH: We are developing methods which will allow us to synthesize copolypeptides and other copolymers which contain side-chain functional groups (e.g. catechol and primary amine) that are present in natural adhesive proteins. It is thought that residue sequence in adhesive proteins may be less important than the functional groups displayed by these polymers. We are preparing a range of different copolymers to probe the effects of the composition and sequence of these functional groups on adhesive and crosslinking behavior. Model studies are also being undertaken to gain mechanistic insight into the roles of the putative active protein components in crosslink formation.

ACCOMPLISHMENTS (LAST 12 MONTHS): Using the known compositions of many natural adhesive proteins, we have prepared statistically random copolypeptides containing the amino acid residues thought to be active in adhesive formation. We have synthesized our copolymers by polymerization of select α-amino acid N-carboxy anhydrides (NCAs) using strong base initiators. We initially prepared binary copolypeptides of L-lysine and L-DOPA containing compositions of the two monomers ranging from 0 to 50 mole percent DOPA. These polymers were found to be soluble in aqueous buffers over a wide pH range (*ca.* 2 -12). We have also prepared ternary copolypeptides containing the amino acids L-serine and L-alanine in addition to DOPA and lysine. The serine and alanine residues were inserted to act as spacers for the functional groups thought to be active in adhesive formation. To analyze crosslinking ability, we monitored the rheological behavior of aqueous solutions of the copolymers as functions of monomer composition, pH, and oxidizing agent. The oxidizing agents utilized were mushroom tyrosinase, O_2, KIO_4, H_2O_2, and $Fe(H_2O)_6^{3+}$. The oxidizing agents were expected to convert the catechol functionalities of the DOPA residues into *o*-quinone units which are believed to be responsible for a variety of crosslinking reactions. By variation of the oxidizing agent and pH, we were able to obtain systems where gel formation times could be adjusted from seconds to hours. In conjunction with these experiments, we have conducted adhesion measurements to correlate gel formation with adhesive strength. Initial measurements using steel and aluminum adherends have shown that molecular oxygen is a very effective oxidizing agent for formation of strong bonds, where cure time can be adjusted by variation of solution pH. In terms of polymer composition, the simple binary copolymer containing lysine (71%) and DOPA (29%)

forms the strongest adhesive bonds with the adherends we have tested so far (tensile shear strength = 1650 psi on aluminum).

SIGNIFICANCE: In work done so far, we have demonstrated that simple binary copolypeptides of statistically random sequence can effectively act as functional mimics of marine adhesive proteins. More detailed studies are clearly necessary, however, our preliminary results indicate that simple polymers bearing catechol and amine functional groups possess good moisture resistant adhesive properties. Another significant outcome of our work has focused on the role of oxidant on crosslink and adhesive formation. We have found that the nature of the oxidant, as well as the reaction conditions used for polymer oxidation, are key parameters for successful adhesive bond formation. In a broader context, our results show that simple, inexpensive copolymers have considerable potential as commercially viable moisture resistant adhesives for both industrial and biomedical applications.

WORK PLAN (NEXT 12 MONTHS): (1) Adhesive strength was found to vary greatly with copolymer composition. It likely also varies with molecular weight. We will prepare copolymers of different molecular weights to analyze this behavior. This information will be combined with our data relating to monomer composition, pH, and oxidizing agents to determine optimized adhesive systems. (2) The test adherends used so far are not the most relevant for potential applications of these materials. We will develop methods for measuring adhesive bonding to more porous and hydrophilic materials (e.g. bone for biomedical applications), and also examine the moisture resistance of these adhesive bonds. (3) We have already begun some mechanistic studies, using small molecules, to probe the reactions of *o*-quinone functional groups with themselves and other species (e.g. primary amines) to understand the adhesive and crosslinking processes. These studies will be pursued in earnest to gain insights into quinone reaction chemistry so that more efficient adhesive materials can be prepared. (4) In effort to further simplify these adhesives, we are preparing catechol and amine functionalized copolymers using inexpensive acrylate and methacrylate backbones. It is expected that the functional side-chains will impart moisture resistant adhesive properties to these wholly synthetic materials as well.

PUBLICATIONS AND ABSTRACTS (LAST 12 MONTHS):

1. Yu, M., DeSimone, T., Deming, T. J. 1997. Synthetic Analogs of Marine Mussel Cement Proteins. Polym. Prepr. *38(1), in press*.